

Superconductivity above 10 K in Non-Cuprate Oxides

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Beginning in 1973, several non-cuprate transition metal and non-transition metal oxides were discovered with superconducting transition temperatures between 10 and 30 K. Retrospectives about these discoveries are given.

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I. INTRODUCTION

The quest for high superconducting transition temperatures T_c led to a slow increase in the maximum observed T_c from 4.2 K in Hg in 1911, which was the discovery of superconductivity itself by Onnes, to 22–23 K in thin films of the cubic A-15 structure compound Nb_3Ge as reported by Gavalier et al. in 1973 and 1974.¹ Oxides and non-transition metal compounds were not seriously considered by most researchers as contenders for high T_c . Superconducting oxides such as NbO and doped SrTiO_3 exhibited $T_c \lesssim 1$ K. The highest T_c oxide, hexagonal rubidium tungsten bronze Rb_xWO_3 , showed $T_c \leq 6.6$ K.² Until 1986, “high T_c ” was considered to be any T_c above 10 K.

Beginning in 1973, a series of discoveries of $T_c > 10$ K in oxides and non-transition metal compounds was made that changed our view of their potential for high T_c . A maximum T_c onset of 13.7 K was discovered by the author and coworkers in 1973 for LiTi_2O_4 with the cubic spinel structure,³ and T_c up to about 13 K was found by Sleight et al. for the non-transition metal oxide $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ with the cubic perovskite structure in 1975.⁴ These T_c s were the highest for oxide and/or non-transition metal compounds until the discovery by Bednorz and Müller in 1986 of superconductivity up to about 30 K in the layered copper oxide compound $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ that contains Cu square lattice layers,^{5,6} as discussed in other chapters by Alex Müller and by Paul Chu. The current maximum T_c of 164 K for this class of compounds was obtained under pressure by Gao et al. in 1994 and is currently also the record T_c for any material.⁷ This T_c was reached by applying 31 GPa pressure to a $\text{Hg}_{1-x}\text{Pb}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ sample that had a zero-pressure T_c of 134 K.⁷ Superconductivity at temperatures up to about 30 K was found in the non-transition-metal cubic perovskite oxide compound $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$ by Mattheiss et al.⁸ and Cava et al.⁹ in 1988. In related developments, bulk high T_c s were discovered by Tanigaki et al. in non-transition-metal alkali metal-doped $A_x\text{C}_{60}$ Buckyballs up to about 33 K in 1991,¹⁰ and in MgB_2 at 39 K by Nagamatsu et al.¹¹ in 2001 as reviewed in a separate chapter by Jun Akimitsu and Takahiro Muranaka. In 2008, the Fe-containing tetragonal compound $\text{LaFeAsO}_{1-x}\text{F}_x$ was discovered by Kamihara et al. to have a high $T_c = 26$ K,¹² as dis-

cussed by Hideo Hosono in another chapter. Members of this general class of materials have crystal structures containing iron square lattice layers with a maximum T_c of 56 K,¹³ which coincidentally(?) is the same transition metal sublattice structure as the Cu atoms have in the layered cuprate high- T_c superconductors.

Herein are presented retrospectives of the discoveries of $T_c > 10$ K in the non-cuprate oxides LiTi_2O_4 , $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$, and $(\text{Ba}_{1-x}\text{K}_x)\text{BiO}_3$, with an emphasis on LiTi_2O_4 because of the author’s familiarity with this compound. Lack of space precludes discussions of their normal or superconducting state physical properties other than their T_c s and of their mechanism(s) for superconductivity.

II. LiTi_2O_4

The face-centered-cubic normal spinel crystal structure of LiTi_2O_4 is shown in Fig. 1 (space group $Fd\bar{3}m$, No. 227). The structure prototype is the mineral spinel with the composition MgAl_2O_4 . The structure consists of a nearly cubic-close-packed array of O atoms layered along the [111] directions of the unit cell, with the Mg atoms in tetrahedral interstices and Al atoms in octahedral interstices between adjacent O layers. The cation sublattices, shown separately in the bottom panel of Fig. 1, are both geometrically frustrated for antiferromagnetic ordering due to the triangular connectivity of the respective nearest neighbors. Most 3d transition metal spinel structure compounds become distorted at low temperatures, which can partially relieve the frustration. There are very few transition metal oxide spinel compounds that remain metallic and cubic at low temperatures. The intermediate-valent spinel compound LiTi_2O_4 is one of these and LiV_2O_4 is another, where the formal oxidation state of both the Ti ($d^{0.5}$) and V ($d^{1.5}$) is +3.5. This nonintegral valence state, together with the undistorted crystal structure, require both compounds to be metals to low temperatures.

The discovery of superconductivity in LiTi_2O_4 came about in the following way. At about the middle of the period (1969–1975) when I was a graduate student at the University of California at San Diego, my research advisor, Bernd T. Matthias, asked me to make a sample of

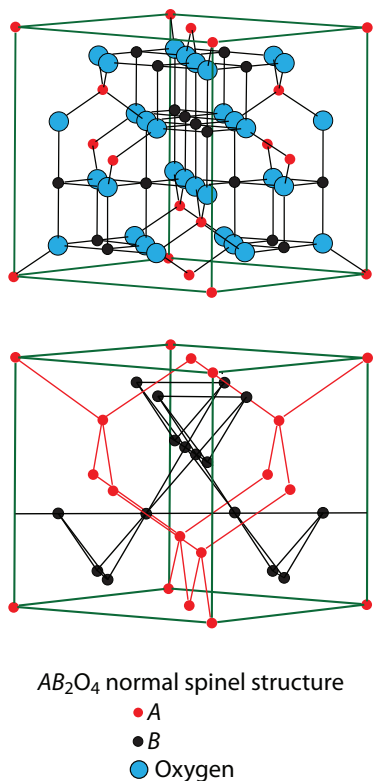


FIG. 1: (Color online) (top panel) Face-centered-cubic crystal structure of a normal spinel oxide compound in which the A atoms occupy only tetrahedral sites and the B atoms only the octahedral sites between O layers that are close-packed along the $[111]$ directions. The unit cell edges are shown. The unit cell contains eight formula units. (bottom panel) Cation sublattice of the normal spinel structure. The B sublattice consists of corner-sharing tetrahedra.

$Li_xTi_{1.1}S_2$, which he and coworkers at Bell Laboratories, Murray Hill, NJ, had recently (1972) reported to become superconducting at a high temperature of 10–13 K for $0.1 < x \leq 0.3$.¹⁴ Lithium is a very reactive alkali metal, so I asked a chemistry professor to make some powder of $Li_xTi_{1.1}S_2$ that I could process further. His postdoc Hari Prakash, using wet chemical methods, provided me with a batch of amorphous $Li_xTi_{1.1}S_2$ which, in retrospect, probably had a high surface area. In order to make a crystalline sample, I wanted to melt it in an arc-furnace (like a commercial arc-welder, but in an inert argon atmosphere). This was certainly not an optimum way to crystallize the material! However, even so, I wanted to do this experiment, so I first poured some of the powder out of the bottle in air in order to make a pressed pellet, but the powder started to smoke! Therefore I made the pellet as fast as possible and loaded it into the arc-furnace. When I tried to melt the pellet, the sample made a lot of smoke that filled up the arc-furnace because of the volatility of Li and S, but it also made a melted round ball that was a beautiful dark blue color (metals are usually silvery and don't usually have colors; pure

bulk elemental Os metal is light blue, though). Then I measured pieces of the blue ball for superconductivity using ac susceptibility measurements and found that the sample became superconducting at 11 K. This seemed to confirm Bernd's findings. But all was not as it seemed. My powder x-ray diffraction pattern of the sample contained lines that I could index as Li_2TiO_3 , and I subsequently found that the intensity of these lines correlated with the volume fraction of superconductivity in similarly prepared samples.

Then, as luck would have it, Bernd had a famous crystallographer friend, Willie Zachariasen, who happened to be visiting Bernd's lab at UCSD at the time. I pointed out to him the set of x-ray diffraction peaks that correlated with the volume fraction of superconductivity. After a couple of days analyzing the peaks, he figured out that the composition of the superconducting material in my samples was close to $LiTi_2O_4$ with a face-centered-cubic (fcc) normal-spinel structure. It turned out that the strongest lines in the pattern were at about the same positions as those for the different phase Li_2TiO_3 noted above. Undoubtedly Hari did provide me with pure $Li_xTi_{1.1}S_2$, but when I exposed it to air, it reacted with the air and oxidized before I could make it into a pellet. Then when I subsequently arc-melted it in pure Ar, part of the sample turned into $LiTi_2O_4$ which was superconducting at 11 K. Furthermore, I later discovered that the metallic spinel structure compound $LiTi_2O_4$ transforms to a semiconducting Ramsdellite structure compound with the same composition upon heating above 950 °C, and that the conversion of the structure to the spinel structure on cooling to below 950 °C is a slow process. Apparently when the melted sample cooled in the arc-furnace, at least some of it converted to the low-temperature spinel crystal structure. The discovery of superconductivity in $LiTi_2O_4$ was thus pure serendipity.

I subsequently learned how to synthesize $LiTi_2O_4$ in a rational way and further confirmed that the superconductivity arose from $LiTi_2O_4$ with the spinel structure at temperatures up to 13.7 K. R. Viswanathan at UCSD carried out heat capacity measurements on the initial samples and demonstrated that $LiTi_2O_4$ is a bulk superconductor. The first announcement of "High-Temperature Superconductivity in the Li-Ti-O Ternary System" was in 1973.³ I did my Ph.D. Thesis on the follow-up synthesis, structure, and properties of polycrystalline samples of $LiTi_2O_4$ and of the solid solution $Li_{1+x}Ti_{2-x}O_4$.^{15–17} Some of these studies were carried out in collaboration with Bill McCallum, Carlos Luengo, Brian Maple, Robert Shelton and Hermann Adrian who were all also at UCSD at the time.

Before I worked on $LiTi_2O_4$, it was known that there exists a complete solid solution of spinel-structure compounds from $LiTi_2O_4$ to $Li[Li_{1/3}Ti_{5/3}]O_4$, which can be written $Li_{1+x}Ti_{2-x}O_4$ with $0 \leq x \leq 1/3$.¹⁵ In this solid solution, some Li substitutes for the Ti on the octahedral sites of the structure. At the same time, the formal oxidation state of the Ti changes from +3.5 to +4.0. The

compound with $x = 1/3$ is a colorless nonmagnetic insulator. Therefore there had to be a metal-to-insulator transition with increasing x . As part of my Thesis work, I investigated this issue and found a metal-insulator transition at $x \approx 0.10$ with T_c being nearly constant for $0 \leq x \leq 0.1$. This suggested that if a metal-insulator transition occurred in a specific materials system, the potential for high T_c superconductivity might be greatest for the metallic compound in that system with a composition closest to the metal-insulator boundary. I made a compilation of oxide and chalcogenide compounds and found that this correlation indeed held about 80% of the time. It was subsequently found to be applicable to the cuprate high- T_c superconductors. This correlation is also mentioned in Arthur Sleight's commentary below. A summary of the literature on LiTi_2O_4 up to 1999 was given by Moshopoulou.¹⁸

Before leaving the topic of LiTi_2O_4 , one might think that the very similar metallic normal spinel structure compound LiV_2O_4 , which has the same beautiful dark blue color, would also be a superconductor. However, in 1973, it was already known that LiV_2O_4 was not superconducting above 4 K, and that this compound, despite being metallic, showed a Curie-Weiss temperature dependence to the magnetic susceptibility with a Curie constant indicating that each V atom had a spin $S = 1/2$ with a spectroscopic splitting factor $g \sim 2$. Since my advisor Bernd Matthias was mainly interested in discovering new superconductors at UCSD, I did not pursue the properties of LiV_2O_4 at that time. It was not until 1997 that my group at Iowa State University discovered that LiV_2O_4 is a very rare example of a d -electron heavy fermion compound, in collaboration with Clayton Swenson and Ferdinando Borsa's and Alan Goldman's groups at Iowa State and with the groups of James Jorgensen, Brian Maple and Yasutomo Uemura.^{19,20}

III. $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$

This compound has a primitive cubic perovskite crystal structure (space group $Pm\bar{3}m$, No. 221), named after the prototype mineral perovskite, CaTiO_3 . The structure is shown in Fig. 2. The structure of an ABO_3 cubic perovskite compound consists of corner-sharing BO_6 octahedra with A atoms in the tunnels between the octahedra. The structure is very susceptible to lattice distortions, sometimes by cooling the cubic structure from room temperature, and many insulating compounds with distorted variants of this structure are ferroelectric.

The following account of the discovery of superconductivity in the $\text{Ba}(\text{Pb}_{1-x}\text{Bi}_x)\text{O}_3$ system at temperatures up to 13 K in 1975 was provided by Arthur Sleight, showing that serendipity was again at work.

"I had just discovered a first-order metal-insulator [MI] transition in $\text{Tl}_2\text{Ru}_2\text{O}_7$ and a second-order metal-insulator transition in $\text{Cd}_2\text{Os}_2\text{O}_7$. I was wondering whether there could be a metal-insulator transition in an

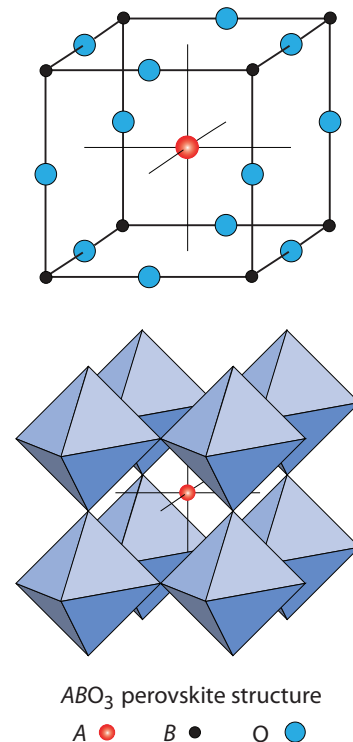


FIG. 2: (Color online) (top panel) Cubic perovskite crystal structure of an ABO_3 compound. The unit cell edges are shown. The unit cell contains one formula unit. (bottom panel) Figure showing the corner-sharing BO_6 octahedra with the A atoms in between. The centers of the eight BO_6 octahedra shown are each occupied by B atoms and are at the corners of the unit cell shown in the top panel.

oxide without a transition metal. BaBiO_3 was known, but it had not been well characterized. The diffraction data that existed at that time suggested that there might be only one type of Bi present. If this were true, BaBiO_3 should be metallic with a half-filled 6s conduction band. I was thinking that as a function of temperature there might be a transition from $\text{BaBi}^{4+}\text{O}_3$ (metal) to $\text{Ba}_2\text{Bi}^{3+}\text{Bi}^{5+}\text{O}_6$ (insulator). I decided crystals were needed, and none have ever been reported. I grew some crystals. At first, I thought they might be metallic because they were a gold color with a metallic luster. However, electrical measurements showed that the crystals were semiconducting with a rather high resistivity. I knew that BaPbO_3 was a very good conductor. So I thought there must be some sort of metal-insulator transition in the BaPbO_3 – BaBiO_3 solid solution, which had never been investigated. I first made 50/50 ($\text{BaPb}_{1/2}\text{Bi}_{1/2}\text{O}_3$). It was not metallic. So I then made $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$, and it was metallic and superconducting. ... I wanted to be very sure of things before we published. I grew crystals of $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ and they were superconducting. We were not set up for magnetic measurements appropriate for superconductors. But I gave a sample to a guy who measured mag-

netic susceptibility. He said it must be a superconductor because the sample jumped out of its holder when the temperature of zero resistivity was reached. I was confident of our results, and I did not want our paper to be reviewed by skeptics. So I sent it to a journal where an Editor would communicate it.⁴ I then tried BaBiO₃–KBiO₃ at that time, but only once and saw no superconductivity.”

“I had previously worked on W and Re oxides superconductors, and I did appreciate at that time that superconductivity frequently occurred in compositions that were close to a phase boundary between metallic and insulating properties. The actual value of T_c in the Ba(Bi,Pb)O₃ system was a surprise to me. So I was not really looking for a new superconductor, but my search for a MI transition based on BaBiO₃ made this discovery inevitable.”

IV. (Ba_{1-x}K_x)BiO₃

Superconductivity was discovered in 1988 at temperatures up to around 22 K in the system (Ba_{1-x}K_x)BiO₃ by Mattheiss et al.⁸ using a specific focused approach. Several factors led to this discovery.⁸ First, the superconductivity at temperatures up to 13 K in the related perovskite system Ba(Pb_{1-x}Bi_x)O₃ described above was well-known. Second, according to Mattheiss, et al., based on previous work, “These results suggest that it should be possible to suppress the ordering waves [that result in insulating behavior] and extend the metallic regime in BaPb_{1-x}Bi_xO₃ closer to the half-filled band condition (BaBiO₃) where the electron-phonon interaction is a maximum, by leaving the conducting Bi-O complex intact and instead doping substitutionally at the inactive

Ba donor sites. This situation, which is analogous to that in La_{2-x}(Ba,Sr)_xCuO₄, is expected to produce marginal stability and enhanced T_c ’s. In earlier studies, a combination of K and Pb doping in a Ba_{0.9}K_{0.1}Pb_{0.75}Bi_{0.25}O₃ sample has produced similar critical temperatures ($T_c \sim 12$ K) but sharper transitions than those observed in Pb-doped BaPb_{0.75}Bi_{0.25}O₃ samples. In the present investigation we have carried out dc magnetization measurements on K-doped Ba_{0.9}K_xBiO₃ samples with $x \approx 0.2$.”⁸ This investigation resulted in superconducting onset temperatures up to about 22 K as noted above.

Cava and coworkers subsequently refined the synthesis procedures and obtained a superconducting onset temperature of 29.8 K in a single-phase cubic perovskite structure sample of Ba_{0.6}K_{0.4}BiO₃, thus firmly confirming the source of the superconductivity as the compound with the cubic perovskite structure.⁹ The onset temperature was determined by Cava et al. from a magnetization measurement of the Meissner effect upon cooling the sample in an applied magnetic field of 19 Oe. We note that direct Meissner effect measurements such as this on other materials are often not informative or conclusive due to flux trapping effects that prevent the magnetic flux from escaping from the sample upon cooling below T_c .

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